Polyacrylamide Gels Filled with Ferromagnetic Anisotropic Powder: A Model of a Magnetomechanical Device

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SYNOPSIS

The concept of a magnetomechanical system able to show permanent magnetization if compressed or to deform in a uniform magnetic field, is presented. The system design is based on polyacrylamide gel filled with demagnetized hard ferrite particles. The ferrite filled gel is deformed by plane strain compression and magnetized while compressed. The orientation of individual magnetized particles was randomized upon compression release. Such samples exhibit no magnetic moment if decompressed and produce magnetic field intensity from 3 to 30 G if compressed. The samples exposed to external uniform magnetic field show macroscopic contraction or expansion of up to 40% of the initial dimensions. The most efficient ferrite was neodymium ferrite in the form of flakes. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

One of the basic properties of plastics is the relative ease of changing their shape by plastic or elastic deformation by directly applying mechanical force. However, the deformation of plastics by other means is rather limited. Most polymeric materials are dielectrics and dia- or paramagnetics because typical elements of organic polymers are dia- or at most paramagnetics. Thus the interaction of conventional polymers with magnetic or electric fields leading to large forces acting on the material is quite limited. By introducing ferromagnetic powders to plastics one may obtain ferroelastics or ferroplastics showing strong interaction with the magnetic field, depending on the concentration of the ferromagnetic powder and the distances between particles.[1] The magnetic remanence and other magnetic properties, like permeability and coercivity, of ferroplastics and ferroelastics depend on the concentration of the ferromagnetic powder, particle shape, sizes, and the distances between particles. For large distances as compared to particle sizes, the interaction with the magnetic field is quite weak due to low concentration of ferromagnetic powder. Such ferroplastics and ferroelastics show poor ferromagnetic properties. If the ferrite particles are close to each other (high concentration of ferromagnetic powder) their magnetic fields interfere, the force lines lock between ferrite particles inside the material, and most of the force lines do not come out of the material; the composite shows high ferromagnetic properties and the assembly of ferrite particles acts as a whole body.[2] However, at high concentration of powder particles the individual particles inside the composite, even those close to the surface of the material, have very little susceptible to the external magnetic field. A carefully balanced concentration of ferromagnetic powder is required for attaining the strong interaction of the external magnetic field with individual particles embedded in a polymer matrix.

The relative change of sizes of typical ferromagnetics due to magnetostriction is on the order of 10^{-6} and it cannot be increased substantially by material modification.[3] Ferroplastics and ferroelastics containing ferrite powders also do not show significantly increased magnetostriction. It is thought that the reason for the low magnetostriction coefficient is the relatively high mechanical modulus of the polymer matrix (usually used low density polyeth-

ylene, chlorosulfonated polyethylene, nitrile rubber, or ethylene–propylene unsaturated copolymers) as compared to the force acting on individual powder particles. The other reason is the high concentration of ferromagnetic powder (usually used concentration ranges between 60 and 95 wt %) that causes, besides the above-mentioned effect of magnetic line force locking, the embrittlement and hardening of the composition due to a high degree of filling. Lowering of mechanical modulus of the composition is possible by a further decrease of the mechanical modulus of the polymer component and the choice of a proper, but low, concentration of a ferrite. One of the possibilities is using polymer gels instead of polymers.

The concept of the studies is to engineer a polymeric material that would show a significant deformation due to the application of an external uniform magnetic field and a recovery upon release of the field, both with the possibility of a frequent repetition. Similar effects of deformation of a material by an outside stimulus were obtained in the past by others in mechanochemical systems,[4,5] thermally activated mechanochemical systems,[6] and electrically activated mechanochemical systems.[7]

The interaction of ferroplastics or ferroelastics with the nonuniform magnetic field is strong due to magnetic field gradients. Besides the rotation of the sample toward the preferred direction of the field, the field gradient also causes the displacement. The gradients of the field cause different parts of the material to be subjected to different forces; hence, the deformation of the sample is possible.

In the uniform magnetic field the only interaction is the moment of couple of the forces that causes the rotation until alignment with the field. In a polymer swollen gel filled with ferromagnetic powder the movement and rotation of ferromagnetic particles would be possible provided that the moment of forces acting on a single particle is sufficient to impose significant deformation of the surrounding gel. The deformation of the polymer gel surrounding individual ferrite particles, if coherent, may superimpose and give rise to a large macroscopic deformation of the filled gel, hence exhibiting the effect similar to large magnetostriction. The interaction of magnetic fields of neighboring particles may also play a significant role.[2]

The goal of the research can be reached by enforcing the coherence of deformation by the procedure presented in Figure 1. The filled polymer gel is subjected to a mechanical compression in a channel die to ensure a plane strain mode of deformation. The compression ratio should be as high as possible, yet not destruct the network of the gel. As a result

of compression the orientation of swollen gel and ferrite particles is obtained. The amount of orientation of the gel around individual particles can be increased by using ferrite particles with a high aspect ratio, for example, particles in the form of needles or flakes. The oriented gel still under compression should then be subjected to a strong magnetic field that will cause permanent magnetization of arranged ferrite particles after magnetic field removal.

The prediction is that, while in the compressed state, the filled gel should show rather strong permanent magnetization. However, the orientation of ferrite particles would randomize if the compression is withdrawn. Then the gel would not show any significant macroscopic magnetization because of the random orientation of otherwise magnetized ferrite particles. However, if the gel is compressed repeatedly the macroscopic magnetization of the gel would show up again due to coherent orientation of magnetized ferrite particles; for example, compressing the gel would cause a development of a permanent magnet. The magnet will disintegrate if the compression is removed.

Moreover, the uncompressed gel subjected to a rather weak magnetic field would deform changing its dimensions toward those assumed by the sample in the compressed state during initial magnetization with the strong field. Again the removal of the field would cause a recovery of the gel to its original dimensions.

EXPERIMENTAL

We have chosen a polyacrylamide hydrogel as a matrix. The samples were prepared by polymerization followed by crosslinking in the following way: 100 g of acrylamide (AA, Roanal, Hungary) was dissolved in 1000 mL of distilled water and 1 g of ammonium persulfate (APS) and 0.5 mL of tetraethylenediamine (TEMED, BDH Chem.) were added without prior purification. The mixture was then polymerized at 48°C for several hours. The obtained viscous water solution of linear polyacrylamide (PAAL) was left for at least 1 week at room temperature prior to further use. Then the required amount of PAAL was supplemented with 40 g/100 mL water solution of AA and 5 g/100 mL water solution of N,N'-methylene–bisacrylamide (BAA, Merck). The relative proportions of PAAL, AA, and BAA were changed in order to obtain a variety of samples of different crosslinking density and different mechanical properties of crosslinked gel. The required amount of ferrite powder was also added and thoroughly dis-
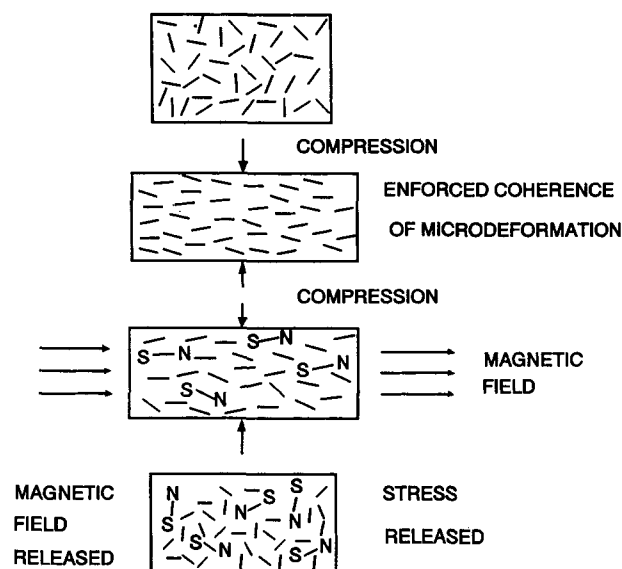
Figure 1 Proposed procedure of magnetization of a compressed ferrite filled gel.

persed by ultrasonication and mixing while heating to 36°C. The crosslinking reaction was initiated by adding APS and TEMED. The amounts of APS and TEMED were determined on the basis of assuring a sufficient induction time of crosslinking, usually 10–30 s, required for proper mixing of all components and reagents. After the induction time a viscous mixture was quickly poured to polymerization forms kept at 36°C. After 2–3 h the samples were removed from the forms and soaked in distilled water for 7–10 days to achieve the equilibrium swelling of the samples. In the case of some ferrites (neodymium ferrites) the soaking period was shortened to a few hours to avoid severe corrosion of the ferrite.

Ten different ferrites were used with the magnetic remanence ranging from 1200 to 8200 G and shapes from irregular grains to flakes with aspect ratio of 5. The following ferrites were used in the studies: barium ferrite FB-1 and FB-4 (Metal Works, Trzebinia, Poland, mean particle diameter respectively 1 and 4 μm, magnetic remanence 3750 G); strontium ferrite $SrO \cdot 6Fe_2O_3$ (Polfer, Poland); manganum ferrite $(Mn, Zn)_y(Fe_2O_3)_{2-Zn}$ (Polfer, Poland); barium-lead ferrite Mag-Guard 3000 (particle size 1–2 μm, magnetic remanence 1200 G, Magnox Inc., Wilmington, DE); barium–strontium–lead ferrite Mag-Guard 4000 (particle size 1–2 μm, magnetic remanence 1500 G, Magnox Inc., Wilmington, DE); strontium ferrite HM 170 and HM 175 (particle size 1.15–1.50 μm, magnetic remanence 2250–2300 G, The Hoosier Magnetics Group, Toledo, OH); neodymium ferrites in the form of flakes, $Nd_2Fe_{14}B$,

MQP-A, and MQP-B (thin flakes $\sim$ 200 μm in diameter, aspect ratio $\sim$ 5, magnetic remanence 7300–8200 G, Magnaquench, a Division of GM, Anderson, IN). All ferrite powders used for preparation of samples were thoroughly demagnetized before embedding in acrylamide by a high frequency demagnetizer of 13.56 MHz at 100 W for 15 min.

Samples for further studies were magnetized after completion of swelling in water in the following way: 20 $\times$ 15 $\times$ 6 mm pieces of filled swollen acrylamide gel were deformed by compression with a plunger in a channel die along a 20 $\times$ 6 mm wall until the compression ratio within the range 1.2–1.5 was reached. The channel die presented in Figure 2 was made from transparent Plexiglas. Then the samples still under compression were magnetized in the uniform magnetic field of 10–12 kG intensity for a few seconds. The magnetic field was slowly decreased until zero intensity and finally the mechanical compression was removed. All experiments with the magnetic field were carried out at room temperature in an excess of water.

RESULTS

Approximately 600 samples were prepared differing in the degree of crosslinking, type of ferrite used, and its concentration ranging from 1 g/100 mL of gel to 150 g/100 mL of gel. The crosslinking reaction
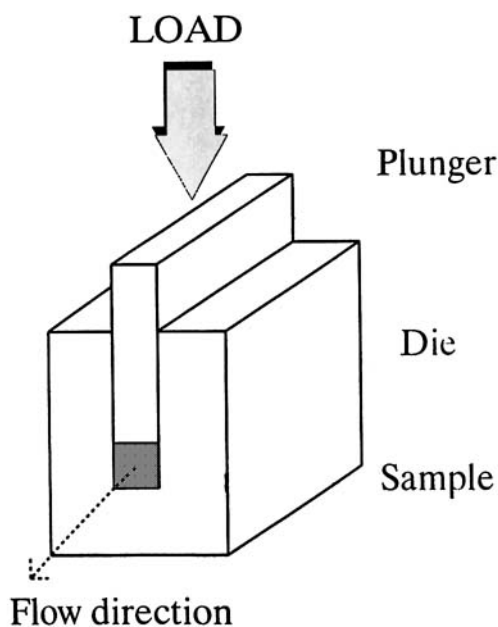

Figure 2 A sketch of a channel die for plane strain compression of ferrite filled gel samples. The channel die and a plunger are made from transparent Plexiglas.

was usually completed within the time interval from several seconds to several minutes. It appeared that it is necessary to limit the time of the crosslinking reaction to 5–15 s only, apart from 10 to 30 s of induction time, to prevent the sedimentation of heavy ferrite particles. For the same reasons it was also necessary to stabilize the temperature of crosslinking at the level of 36°C. The crosslinking reaction of PAAL is greatly accelerated in the presence of all neodymium ferrites as compared to polyacrylamide containing other ferrites and not containing any filler. Hence, the typical compositions of reagents for various ferrite powders were different. The best composition for obtaining good mechanical properties of a gel and acceptable crosslinking time are presented in Table 1 for three exemplary ferrites used. No significant sedimentation of ferrites was observed during the crosslinking reaction due to high viscosity of the reacting mixture and short time of reaction: approx. 15 s in the case of FB-1 ferrite, approx. 15 s in the case of Mag-Guard 4000, and 6–7 s in the case of MQP-A and MQP-B. The procedure of crosslinking described in Experimental delivered mechanically consistent filled gel providing that the composition of reagents was carefully chosen for a particular ferrite. MQP series filled gels soaked for short period of time (2 h) showed almost no additional water intake.

Usually the crosslinking reaction was apparently completed within several tens of seconds while in the case of neodymium ferrites the time was only 6–7 s. The sedimentation of ferrite particles was negligible during crosslinking time. Soaking of freshly polymerized gels in distilled water over a period of 5–7 days led to the absorption of 5–30% of additional water depending on the crosslinking degree: less crosslinked gels absorb more water from approx. 10 wt % for FB-1 ferrite to 7% for MQP-A ferrite filled gel. Saturation of water sorption was usually reached within 1–2 days.

Gel compositions prepared according to Table I were characterized by good mechanical consistency, a wide elastic response to compressive deformation, and ability to withstand a high degree of deformation up to 50–100%. More crosslinked gels can be compressed without fracture to a smaller compression ratio; less crosslinked gels showed a shallow elastic response.

Gels filled with ferrite particles and crosslinked according to Table I were compressed in the channel die and subjected to a uniform magnetic field of 10 kOe intensity while under compression. When the magnetic field was withdrawn, but not the compression, the gels exhibited permanent magnetization of 3–30 G at the poles depending on the concentration and the type of ferrite dispersed in the gel. Then, when the compression was removed, all samples recovered to their initial dimensions before compression and magnetization. The samples prepared in this way possess uniformly magnetized particles in the deformed state; but after removal of compressive stress, the particles recovered to their initial positions and their orientation was randomized. This effect was particularly well pronounced in MQP-A and B ferrite powder; compressed and then magnetized ferrite gels show almost no permanent magnetic moment if decompressed. In most cases the field at the former poles was below 0.1 G. However, each time the magnetized ferrite gel is compressed, in the way it was compressed during initial magnetization, a magnetic field appears with the intensity at poles of 3–30 G depending on the concentration and magnetic remanence of the ferrite used. The creation of the magnet is explained in Figure 3. Compression applied to the gel in the same way as during initial magnetization causes the reconstruction of the orientation of individual ferrite particles and the magnetized ferrite particles assume spatial coherence of their magnetic moments. The assembly of ferrite particles produces now an outside

Table I Best Compositions of Reagents for Obtaining Polyacrylamide Gel Filled with Exemplary Ferrites

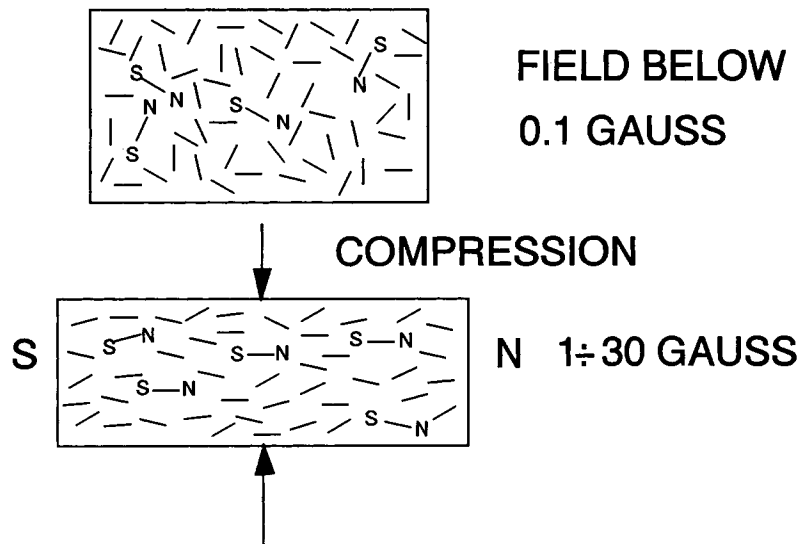|	FB-1 (Poland)	MAG-GUARD 4000 (Magnox)	MQP-A (Magnaquench)
80 g H_2O + 40 g AA + 2 g BAA	1.0 mL	1.5 mL of	1.5 mL
PAAL	2.5 mL, 10% in H_2O	2.0 mL, 10% in H_2O	7.5 mL, 10% in H_2O
APS	0.1 g	0.1 g	0.1 g
TEMED	150 μL	50 μL	50 μL
H_2O	6.5 mL	5.5 mL	5.5 mL
Ferrite	0.1–1.0 g	0.1–1.0 g	0.5–1.0 g

Figure 3 Formation of a permanent magnet by compression of formerly magnetized, compressed ferrite filled gel.

magnetic field of 1–30 G intensity at the poles. The observable effect of the creation of a permanent magnet by mechanical compression is a direct transformation of the mechanical work into magnetic field energy. The cycle of a compression associated with the creation of a magnet can be repeated several hundred times without apparent damage to the gel if the compression ratio does not exceed the compression ratio applied during magnetization.

The same samples, subjected to a uniform magnetic field of less than 500 G of intensity along the direction of initial magnetization, show the change in dimensions related to the magnetic field intensity, the concentration of a ferrite, and its magnetic remanence, but never exceed the ratio applied during initial magnetization, for example, 1.5. The highest achievable deformation ratio was 1.4 for the case of MPQ-A and MPQ-B ferrites. The example of deformation of a polyacrylamide gel filled with 3 wt % barium ferrite (FB-1 ferrite magnetic remanence 3750 Oe) is presented in Figure 4 as a function of an increasing magnetic field intensity. This is an example of a direct transformation of magnetic field energy into mechanical work of gel deformation.

The deformation of the samples subjected to a uniform magnetic field occurs usually within a few hundredths of a second; the recovery to previous dimensions after field removal needs a few seconds and depends on the crosslinking degree of the acrylamide gel, water, and filler concentrations.

Dependence of deformation on field intensity is presented in Figure 5 for the 5 wt % neodymium

ferrite in the form of flakes (MPQ-A ferrite) in polyacrylamide gel. The initial straight slope extends over 300 G of the field intensity followed by a saturation at approximately 400 G. For other samples the dependence of field intensity at saturation on the concentration of ferrite particles is not equivocal: similar deformations are obtained for low and high concentrations of ferrite. However, the best results were obtained for the 5 wt % ferrite in the gel. Such behavior results probably from the interaction of magnetic fields of neighboring ferrite particles. On the other hand the magnetic field intensity at saturation of deformation is higher for the more crosslinked gel with its lower water content, lower magnetic remanence of ferrite powder, and lower aspect ratio of ferrite particles.

The cycle of application and removal of the magnetic field in the range below saturation can be repeated more than a few hundred times without apparent damage to the filled gel. Some small amount of water is exuded from the sample each time the sample is deformed by the magnetic field and slowly absorbed upon recovery without the field.

Observation of the samples subjected to a magnetic field by stereo light microscope revealed rotation of each of the ferromagnetic particles toward the direction of lines of force of the applied magnetic field. Upon field removal the particles recovered to their initial positions. No decohesion between ferrite particles and the gel was observed below the field intensity of saturation in most cases. If the field exceeded saturation (in most cases above 500 G) the alignment of ferrite particles with the field lines was
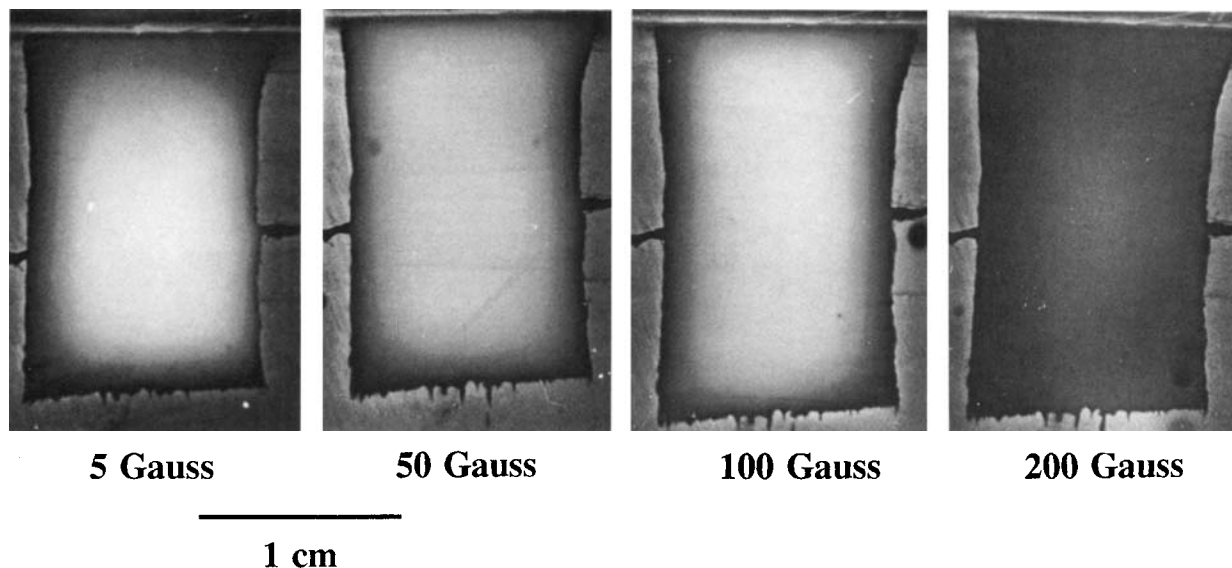
5 Gauss   **50 Gauss**   **100 Gauss**   **200 Gauss**

1 cm

Figure 4 A series of photographs illustrating the deformation of a polyacrylamide gel filled with 3 wt % barium ferrite (FB-1, Metal Works, Trzebinia, Poland) subjected to a uniform magnetic field of increasing intensity. The sample was magnetized earlier in the uniform magnetic field of 10 kOe intensity while being compressed in a channel die to the compression ratio of 1.5.

complete and the displacement of ferrite particles was observed, such that the contacts between the particles and the gel often break. This is probably due to some field gradients caused by the inhomogeneities of the field, the laboratory system, and slightly nonhomogeneous dispersion of ferrite particles. Such samples were then unable to deform significantly again due to a weak magnetic field (i.e. below 500 G). The damage to the filled gel does not occur at high magnetic field intensity if the sample is compressed in a channel die during exposure to the strong magnetic field.
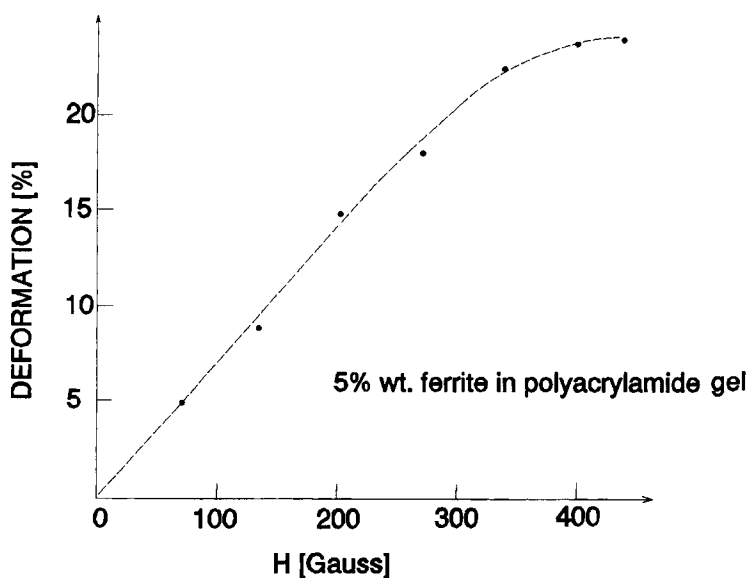

Figure 5 Dependence of deformation of polyacrylamide gel filled with 5 wt % neodymium ferrite (MQP-A, Magnaquench) on the magnetic field intensity. The sample was magnetized earlier in the uniform magnetic field of 10 kOe intensity while being compressed in a channel die to the compression ratio of 1.5.

CONCLUSIONS

Polyacrylamide hydrogel filled with ferrite particles during polymerization magnetized in a deformed state shows several intriguing phenomena:

1. no permanent magnetization if deformation is removed;
2. permanent magnetization with the field intensity of 3–30 G at poles if deformed and recovery to no magnetization if deformation is removed;
3. deformation if subjected to a uniform magnetic field;
4. recovery to initial dimensions if the magnetic field is withdrawn;
5. the procedures mentioned above can be repeated more than a few hundred times without apparent damage to the gel.

The filled gel that undergoes shape change and develops contractive forces in response to an outside stimulus by external magnetic field may be called a "magnetomechanical system." This system is capable of directly transforming the magnetic field energy to mechanical work and conversely of transforming mechanical work into magnetic field energy. The presented experiments demonstrate the feasibility of various types of actuators, such as magnetic valves, on-off switches, models of an artificial muscle, etc. that may be constructed from such types of ferrite filled hydrogels.

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